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(54) Insecticide treatment and compositions therefor.

(57) Fabrics, especially furnishing fabrics, the threads of which are coated with a film of a polymeric substance incorporating an insecticidally active substance. The fabrics are particularly useful for making up into articles such as curtains, bed-nets and the like.

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INSECTICIDE TREATMENT & COMPOSITIONS THEREFOR

This invention relates to treatment of fabrics with insecticides and compositions for use in the treatment, and to fabrics thus treated.

Among the uses of insecticides for arthropod control, the pyrethroid insecticides have become popular for "impregnation" of fabrics such as carpets, curtains and mosquito nets. The pyrethroids include chemicals such as permethrin, cypermethrin and lambda-cyhalothrin which are very stable and insecticidal. These chemicals, usually formulated as emulsion concentrates for aqueous dilution, can be conveniently and safely used for residual treatment of materials requiring to demonstrate a prolonged insecticidal effect.

The use of pyrethroid insecticides for "impregnation" of mosquito nets and curtains as a means of killing mosquitoes and other flies that settle on the treated materials is well known. This concept is based upon the way that blood-sucking arthropods may contact the insecticide-treated substrate when attracted to a nearby host, eg. a person sleeping under a bednet. This promotes the control of the pests, eg. mosquitoes.

Because people tend to wash their bednets, curtains, etc. from time to time, it is desirable to enhance the persistence of insecticides on treated materials by making them wash-proof, to some extent. However conventional insecticidal compositions do not provide a washproof insecticidal effect and the present invention is concerned with a solution to this problem.

Accordingly the present invention provides a method of treating fabrics to impart washproof insecticidal properties thereto which comprises treating said fabric with a insecticidally effective amount of a liquid composition comprising an insecticidal active ingredient and a polymeric substance. The threads of the treated fabric are thus coated not only with the insecticidal active ingredient but also with the polymeric substance. The effect of the polymeric substance is to increase the adhesion of the insecticidal substance to the fabric by incorporating the insecticidal substance in a film of the polymeric substance, which itself adheres to the individual threads of the fabric. The invention thus provides woven or non-woven fabric material the threads of which are coated or partially coated with a film of an adherent polymeric substance incorporating an insecticidally active substance. The fabric may be in the form of furnishing fabrics, such as curtains, bed-linen, bed-nets, furniture covers, or may be incorporated into matting, carpets or other floor covering. Alternatively the fabrics may be made up for use in packaging, such as sacks for the storage and transport of materials, including foodstuffs subject to spoilage by insect pests.

Fabrics to be treated may be made of natural fibres such as cotton, raffia, jute, flax, sisal, hessian, or wool, or synthetic fibres such as polyamide, polyester, polypropylene, polyacrylonitrile or the like.

The method of the invention may be practised using liquid compositions comprising any suitable insecticide which is effective against the pests to be controlled, particularly adult mosquitoes and flies. Thus the insecticide may be carbamate such as propoxur or bendiocarb, or an organophosphorus insecticide such as malathion, pirimiphos-methyl or fenitrothion, or a pyrethrin or pyrethroid insecticide such as allethrin, bioallethrin, S-bioallethrin, neopynamin, fenvalerate, permethrin, cypermethrin, alphamethrin, deltamethrin, cyhalothrin or lambda-cyhalothrin.

The compositions may be of any suitable liquid solvent based type, for example, emulsifiable concentrate (EC), oil-in-water emulsions (EW), which are applied after dilution with water, or solutions which may be applied directly by ultra-low volume spraying.

The compositions also comprise a polymeric substance, dissolved in the liquid solvent. This may be a natural resin or wax such as wood rosin, ester gum, paraffin wax or shellac. Shellac is particularly useful. The polymeric substance may also be a synthetic polymer, such as polyethylene, polypropylene, an ethylene/vinyl acetate copolymer, polystyrene, a styrene/butadiene copolymer, polyacrylonitrile, a copolymer or acrylonitrile, butadiene and styrene, polyvinyl chloride, an acrylate polymer such as polymethylmethacrylate, or a polyamide. The molecular weight of the polymer must be such that required concentration in the composition can be obtained by dissolution in the solvent. Thus polystyrene having an average molecular weight within the range from 2000 to 1000000 is particularly useful. In general the average molecular weight of the polymer should be such as to permit ready dissolution in the solvent used in the composition, and at the same time provide significantly increased washfastness of the insecticide deposit on the fabric. In order to ensure that good adhesion is obtained for a particular combination of fibre and insecticide it may be helpful to combine more than one polymer in a blend. The solvent can be any suitable organic solvent in which the insecticidal active ingredient in soluble, and in which the polymeric substance is simultaneously soluble. Suitable solvents include ketones such as cyclohexanone, iso-phorone, acetophenone, and methylisobutyl ketone, ethers such as anisole, esters such as hexyl acetate and methylbenzoate, vegetable oils, amides such as N-methylpyrrolidone, chlorinated hydrocarbons such as

1,1,1-trichloroethane, chloroparaffins and chlorotoluene, aromatic carbons such as alkyl benzenes and methylnaphthalene, aliphatic hydrocarbons such as alkylcycloparaffins, branched-chain alkanes and alcohol-ethers such as diethylene-glycol mono-methyl ether, propylene glycol mono-methyl ether, polyethylene glycol and tetrahydrofurfuryl alcohol, or mixtures thereof.

The compositions may also contain wetting emulsifying or dispersing agents, which may be of the cationic, anionic or non-ionic type. Suitable agents of the cationic type include, for example, quaternary ammonium compounds, for example, cetyltrimethyl ammonium bromide. Suitable agents of the anionic type include, for example, soaps, salts of aliphatic monoesters or sulphuric acid, for example, sodium lauryl sulphate, salts of sulphonated aromatic compounds, for example, sodium dodecylbenzene-sulphonate, sodium, calcium or ammonium lignosulphonate, or butylnaphthalene sulphonate, and a mixture of the sodium salts of diisopropyl- and triisopropylnaphthalene sulphonates. Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol or cetyl alcohol, or with alkyl phenols such as octyl phenol, nonyl phenol and octyl cresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, and the lecithins.

The compositions which are to be used in the form of aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient or ingredients, the said concentrate to be diluted with water before use. These concentrates are often required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water to form aqueous preparations which remain homogenous for a sufficient time to enable them to be applied by dipping or by conventional spray equipment.

The compositions may contain from 1 to 70% by weight of the insecticidal active ingredient, and preferably from 5 to 50% by weight. They may also contain from 1 to 25% by weight of the polymeric substance, and preferably from 3 to 15% by weight. In other respects the compositions resemble conventional compositions of insecticides of the emulsifiable concentrate, oil-in-water emulsion, or solution type.

Where the composition is diluted with water before use it may be applied to the fabric by direct spraying, or by dipping or soaking the fabric in a bath containing the diluted composition. The fabric may be finished and made up fabric, such as curtains (particularly net curtains), bed-linen, furniture covers or the like, or may be new fabric. In the latter case the insecticide treatment may be carried out at the end of the manufacturing process, by placing the insecticidal composition in the final treatment bath.

The leaching of insecticides from fabrics during the washing process not only reduces the insecticidal effectiveness of the deposit on the fabric, but also allows the insecticides to pass into the wash water. Although this does produce an environmental hazard where individual fabrics such as bednets are washed from time to time in the course of a normal domestic laundry regime, a problem can occur if treated fabrics are routinely washed during continous manufacturing processes. Thus insecticides are frequently applied to fabrics used in carpet manufacture for the control of carpet beetles, but in subsequent treatments during manufacture some of this may be washed out of the carpet, leading to a potential hazard to the environment if the wash waters are subsequently discharged into natural waterways. By the use of the invention method and compositions the amount of insecticides washed out of the carpet may be significantly reduced.

The invention is illustrated by the following Examples. The examples illustrating compositions of particular active ingredients may be considered as exemplifying also compositions in which the active ingredient is replaced by others of similar effectiveness.

EXAMPLE 1

This Example illustrates an emulsifiable concentrate according to the invention.

	% w/w
Cypermethrin	25
Polystyrene	5
Calcium dodecyl benzene sulphate	5
'Synperonic' NP13	5
'Solvesso' 200	to 100

'Synperonic' NP13 ('Synperonic is a registered trade mark) is a condensate of nonylphenol with ca. 13 moles of ethylene oxide.

'Solvesso' 200 ('Solvesso is a registered trade mark) is a blend of methylnaphthalenes.

The polystyrene has an average molecular weight of about 100000.

EXAMPLE 2

This Example illustrates an emulsifiable concentrate according to the invention.

	% w/w
Lambda-cyhalothrin	5
Polystyrene	10
'Synperonic' OP10	7
Calcium dodecyl benzene sulphonate	3
'Solvesso' 100	to 100

'Solvesso' 100 ('Solvesso' is a registered trade mark) is a solvent blend of C_9-alkylbenzenes.

EXAMPLE 3

This Example illustrates a solution suitable for ultra-low volume spray application.

	% w/w
Permethrin	5
Shellac	5
'Aromasol' H	to 100

'Aromasol' H ('Aromasol' is a registered trade mark) is a solvent blend of xylenes and ethylbenzene.

EXAMPLE 4

This Example illustrates an emulsifiable concentrate suitable for use in the method of the invention.

	% w/w
Pirimiphos-methyl	25
Polystyrene	5
'Synperonic' NP13	5
Calcium dodecyl benzene sulphonate	5
Epoxidised soya bean oil	4
'Solvesso' 100	to 100

EXAMPLE 5

This Example illustrates two further emulsifiable concentrates suitable for use in the method of the invention

(a)	%
lambda-cyhalothrin	2.5
Polystyrene (M.W. 10^5)	5.0
'Tensiofix' B7416	4.0
'Tensiofix' B7453	6.0
'Cereclor' 63L	24.0
'Solvesso' 100	to 100.0
(b)	
permethrin	25.0
Polystyrene (M.W. 10^5)	5.0
'Tensiofix' B7416	4.0
'Tensiofix' B7453	6.0
'Cereclor' 63L	6.8
'Solvesso' 100	to 100.0

'Tensiofix' B7416 and B7453 (Tensiofix' is a Registered Trade Mark) are blends of surface active agents.

'Cereclor' 63L ('Cereclor' is a Registered Trade Mark) is a blend of chlorinated paraffinic solvents.

EXAMPLE 6

This Example illustrates the washfastness obtained by the method of the invention. The composition of Example 1 was used and compared with a similar composition omitting the polystyrene (control). Nylon mosquito netting samples (10 x 10 cm) were dipped into a bath containing the diluted composition until a loading of 0.4g/m^2 of permethrin was obtained. After drying the netting was used to demonstrate insecticidal effect against Anopheles gambiae mosquitoes after 0, 1 and 2 washings with soap. The results, which are given as the mean percentage mortality and mean percentage knock-down of three replicates, show that the use of polystyrene in the composition gives an approximately threefold better effect after one wash and an approximately sixfold better effect after two washes than the control. Results are also given for a similar composition in which the polystyrene is replaced by Shellac which also showed a significant increase in washfastness as compared with the control.

Polymeric Substance	% Mortality (% Knockdown) after		
	0 Wash	1 Wash	2 Washes
Polystyrene	90.5 (95.2)	92.9 (100)	68.8 (100)
Shellac	84.1 (95.5)	44.0 (62)	39.3 (24.6)
None	93.0 (74.4)	25.0 (31.3)	9.5 (4.9)

EXAMPLE 7

This Example illustrates two emulsifiable concentrates according to the invention, A and B, and compares the washfastness of the insecticide deposit on nylon (polyamide) netting with that obtained from a conventional insecticidal composition, C.

Ingredient	% wt		
	A	B	C
Permethrin	25.0	25.0	25.0
'Arylan' CA	7.5	7.5	7.5
'Triton'X100	12.5	12.5	12.5
Polystyrene	10.0	5.0	-
'Aromasol' H	to 100.0	to 100.0	to 100.0

'Arylan' CA ('Arylan' is a Registered Trade Mark) is calcium dodedecylbenzene sulphonate.

'Triton' X100 ('Triton' is a Registered Trade Mark) is a condensate of octylphenol with 10 moles of ethylene oxide.

Nylon samples were treated with the compositions according to the method of Example 6 and divided into three groups for each composition. The first group was not washed, the second group washed once, and the third group washed twice. The residual deposit of insecticide in each group was then determined by a gas-chromatographic technique in which the deposit was first removed by dissolution in chloroform, using a Hewlett Packard 5880 gas chromatograph, equipped with a 25m x 0.2mm (i.d) fused silica methyl-silicone (CP sil 5CB) column, at 60°C (initial) to 240°C (final) and an injection temperature of 280°C. The results are given in the following table (expressed as mg/m^2 of permethrin retained on the netting) and show clearly that the incorporation of the polystyrene significantly increases the washfastness of the permethrin deposit.

No of Washes	A	B	C
0	580	425	325
1	390	150	11
2	260	130	4

Claims

1. Woven or non-woven fabric material the threads of which are coated or partially coated with a film of an adherent polymeric substance incorporating an insecticidally active substance.

2. Fabric material according to claim 1 made of natural fibres selected from cotton, raffia, jute, flax, sisal, hessian and wool, or synthetic fibres selected from polyamide, polyester, polypropylene or polyacrylointrile fibres, or a blend of any such natural and synethetic fibres.

3. A method of treating fabrics to impart washproof insecticidal properties thereto which comprises treating said fabric with an insecticidally effective amount of a liquid composition comprising an insecticidal active ingredient and a polymeric substance.

4. A method according to claim 3 wherein the insecticidal active ingredient is a pyrethroid, a carbamate or an organo-phosphorus compound.

5. A method according to claim 3 wherein the polymeric substance is polystrene, or Shellac.

6. A method according to claim 3 wherein the fabric is an open-meshed netting.

7. Fabric treated by the method of claim 3.

8. A method of combating insect pests in a dwelling which comprises suspending a fabric according to claim 1 in the dwelling such that it is accessible to the insect pests.

9. A composition for use in the method of claim 3 which comprises as insecticidally active ingredient a pyrethroid and a polymeric substance, in solution in an organic solvent, and, optionally, additionally comprising surface active agents.

10. A composition according to claim 9 wherein the insecticidally active ingredient is selected from permethrin, cypermethrin, alphamethrin, deltamethrin, allethrin, fenvalerate, cyhalothrin, or any isomer or mixture of isomers thereof.

11. A composition according to claim 9 wherein the polymeric substance is selected from polystyrene and shellac.

12. A composition according to claim 11 wherein this polymeric substance is polystyrene having an average molecular weight in the range 2000 to 1000000.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 90300847.2

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
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Y	EP - A1 - 0 010 630 (SAREA A.G.) * Claims * --	1,3,5, 11,12	
X	EP - A1 - 0 170 611 (CIBA-GEIGY) * Claims 1,5,7,10-14; page 6, lines 1-8 * --	1-4, 7-10	
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 180, no. 180, July 25, 1985 THE PATENT OFFICE JAPANESE GOVERNMENT, page 120 C 293 * Kokai-no. 60-51 101 (TOPPAN INSATSU K.K.) * --	1-4, 7-10	TECHNICAL FIELDS SEARCHED (Int. Cl.)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	30-04-1990	SCHÄFER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl.5)
X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C section, vol. 3, no. 19, February 17, 1979 THE PATENT OFFICE JAPANESE GOVERNMENT, page 44 C 37 * Kokai-no. 53-142 523 (SUMITOMO KAGAKU KOGYO K.K.) *	1,3-5, 11,12	
			TECHNICAL FIELDS SEARCHED (Int Cl.5)

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